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THESIS

THE MOLECULAR ADSORPTION AREAS of HYDOCARBON GASES ON COCONUT CHARCOAL

by

V.J. MacCosham, B.Sc.

University of Alberta,

Department of Chemistry

April, 1953.

THE MOLECULAR ADSORPTION AREAS

of

HYDROCARBON GASES ON COCONUT CHARCOAL

Submitted in Partial Fulfillment
of the Requirements for the
Degree of Master of Science.

by

V.J. MacCosham, B.Sc.

Under the direction of Dr. J.L. Morrison

Edmonton, Alberta. April, 1953.

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INTRODUCTION

Introduction

Adsorption is a process in which molecules or atoms are bound to the surface of a substance. The former is known as the adsorbate and the latter, the adsorbent. The magnitude of the forces which bind the adsorbate to the adsorbent constitutes a criterion for differentiation between physical adsorption and chemisorption. The former is characterized by a weak interaction between adsorbate and adsorbent, and is sometimes known as "Van der Waals" adsorption, which implies forces involved similar to those encountered in condensation. Chemisorption involves energies similar to those found for chemical reactions.

Because the sorption of gases on charcoals usually involves physical adsorption, the term adsorption, as used here will refer only to physical adsorption.

Adsorption is a function of many variables: time; pressure or concentration; temperature; and nature of the adsorbate and adsorbent. The determination of an adsorption isotherm eliminates the temperature variable. However, the nature of the adsorbate and the time variable may be complicating factors.

Usually, pressure or concentration is the variable in the determination of an isotherm. This is only strictly correct for adsorbents which present the same surface areas to various gases. Such a condition seems most likely to be encountered with non-porous adsorbents. However, Emmett (1), and, Beebe, Beckwith, and Honig (2), have cast some doubt on this presumption. They have indicated that the same non-porous adsorbent areas are not equally available to large and small molecules. They explain the variation on the basis of differences in packing of the adsorbate molecules.

A porous adsorbent presents an entirely different situation. The larger portion of the surface area of such a substance constitutes the walls of the pores. These pores vary greatly in size and present a major problem in the measurement of surface area. That is; the larger pores can be entered by a variety of different sized molecules, whereas the smaller ones will exclude the larger molecules from access to their internal surfaces. This is known as seiving, or screening. The accessibility of the gas molecule to the internal surfaces of these pores is dependent upon whether the molecule is horizontally or vertically oriented, as proposed by Nay and Morrison (3). They suggest that in the case of horizontal orientation, molecular thickness governs the screening effect as opposed to molecular length in the case of vertical orientation.

An outgrowth of the seiving effect is the use of molecular size as a criterion of pore size or vice-versa. However, the effects of screening and molecular packing are not separable, particularly for larger adsorbate molecules and for smaller pores. The effect of molecular size as shown by comparison of the amounts of various gases adsorbed can give some idea of the pore distribution.

Activation may be described as a process by which the surface area of the adsorbent is increased. A coconut charcoal is usually activated by steam at high temperatures and pressures. As activation proceeds, the distribution and size of pores changes. It has been shown by Fineman, Guest, and McIntosh (4) that the lower activated charcoals have a larger proportion of finer pores. This is in agreement with the findings of Nay and Morrison. The latter have shown that at higher activations a variety of different sized molecules have access to the same internal surfaces.

The average area of an adsorbate molecule in a monomolecular film on the surface of the adsorbent is known as the effective adsorption area of the molecule.

The calculation of the adsorption areas of various molecules and the concomitant surface area calculations of the adsorbent may be carried out in numerous ways, dependent upon which method gives the best agreement with the data on hand. In this particular case, the Langmuir equation was found to afford the best treatment. A form of this equation is:

$$\frac{P}{V} = \frac{1}{V_m b} + \frac{P}{V_m} \qquad (1)$$

where: P = equilibrium pressure

V = volume of gas adsorbed

V_m = volume of gas required to form a monolayer

b = constant

A plot of P/V versus P will be linear, of slope $1/V_m$, and with an intercept of $1/V_m b$.

Nay and Morrison also made use of this relationship. However, they noticed that the isotherms obtained possessed a slight curvature, concave to the pressure axis. The curvature was more pronounced with the lower activated charcoals and with the larger adsorbate molecules. In order to account for the curvature in the Langmuir plots, they suggested that two processes were occurring simultaneously; adsorption and diffusion of the adsorbate into the finer pores of the adsorbent. They attempted to resolve these processes by the use of a pressure versus time graph for each point on the isotherm. The accompanying figure indicates the general type of curve they obtained.

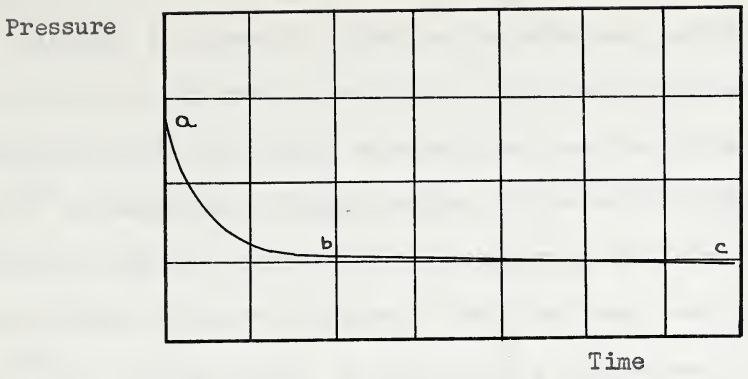


Fig. 1

The region a to b was considered by them to represent both processes, but mainly adsorption. The region b to c was considered to be mainly diffusion. Accordingly, they selected b as the end point of the adsorption process.

In order to measure molecular adsorption areas, V_m, the volume of gas required to form a monomolecular film on the surface of the adsorbent is obtained from the slope of the Langmuir isotherm. Then the relationship:

$$\sigma = \frac{V'_m}{V_m}\,\sigma' \qquad (2)$$

where: V'_m = volume of a reference gas required to form a monolayer.

V_m = volume of gas under investigation required to form a monolayer.

σ' = adsorption area of reference gas.

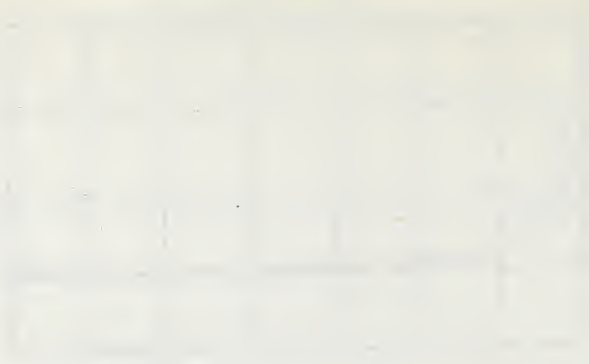
σ = adsorption area of gas under investigation.

is used to calculate molecular adsorption areas.

Nay and Morrison have made the following observations regarding the lower activated charcoals.

(1) Molecules thinner than the reference gas reach larger internal surfaces, resulting in lower adsorption areas as compared with the correct ones.

(2) Molecules thicker than the reference gas do not reach the same internal surfaces, resulting in larger adsorption areas than the correct ones.



Nitrogen is generally chosen as the reference gas because its adsorption area is accurately known. An absolute calorimetric method developed by Harkins and Jura (5), yields an adsorption area for molecular nitrogen of 16.2 $\mathring{A}^2$ on the basis of liquid packing at the boiling point of liquid nitrogen (-196°C). This value is in agreement with that arrived at by many others using a variety of methods. There has been some indication that 15.4 $\mathring{A}^2$ is a better value. Livingston (6), reviews much of the recent work in this field and indicates that 15.4 $\mathring{A}^2$ is the better value.

The purpose of this thesis is to carry out the measurements of the adsorption of a number of hydrocarbon gases on a series of coconut charcoals of different degrees of activation. The work described here is a continuation of that reported by Nay and Morrison (3), and includes the following original material:

(a) In addition to nitrogen, methane, propane, butane, isobutane, and acetylene which were studied by Nay and Morrison, measurements were made with propylene, butadiene-1,3, cyclopropane, and neopentane.

(b) A different series of activated charcoals was used.

(c) The equilibrium times were studied throughout.

(d) The isotherms were measured at lower pressures.

EXPERIMENTAL

Experimental

I Materials

The charcoals used were a series of steam activated coconut shell charcoals derived from the same initial charge, and which were activated for different lengths of time.

Chemically pure helium, propane, propylene, butane, isobutane, and cyclopropane were obtained from the Ohio Chemical Co. The helium was further purified by passage through an activated charcoal trap immersed in liquid air prior to entry into a storage bulb. The other gases were purified further by fractional distillation.

Pure grade butadiene-1,3,, and neopentane were obtained from the Phillips Petroleum Co. The butadiene-1,3 contained 0.02% tertiary butyl catechol which acted as a polymerization inhibitor. It was removed, prior to fractionation and storage by passage of the gas through 40% aqueous caustic soda followed by several drying towers containing the same material. Previous to its use, neopentane was fractioned.

Tank acetylene was used subject to purification after the manner described by Farkas and Melville (7).

Methane was prepared by hydrolysis of methylmagnesium iodide and purified as described by Farkas and Melville.

The nitrogen used was oil-pumped tank nitrogen which was further purified by passage over the following in the sequence given: Dehydrite; copper deposited on glass wool, at 400 - 450°C; copper oxide deposited on glass wool, at 400 - 450°C; Dehydrite; and finally activated charcoal at the temperature of liquid air.

The copper and copper oxide were deposited on pyrex glass wool by allowing the glass wool to soak for a period of time in a saturated solution of cupric nitrate in ethanol. The glass wool was removed and the excess ethanol was ignited. The residue was then baked until brownish black. Two portions

of the residue were alternately oxidized and reduced several times at 400 - 450°C using oxygen and hydrogen respectively. Between oxidations and reductions, the system was flushed out with nitrogen to reduce the explosion hazard. One portion was left in the oxidized state and one in the reduced state.

It was found that the Apeizon stopcock greases were not suitable for this work since some of the hydrocarbon gases were soluble in them. Cello-Grease (No. 14 - 637); manufactured by the Fisher Scientific Co., was found to be satisfactory.

II Apparatus

The apparatus used was similar to that described by Emmett (8), and almost identical to that used by Nay and Morrison (3). A glass mirror scale for reading pressures was used in the later part of the work. Previously, a calibrated wood meter stick had been used.

III Method

Manipulation of the apparatus and a description of the calculations are given by Emmett (8).

Samples of 0.20 to 0.25 grams of charcoal (dry weight) were used. They were degassed at 250 - 300°C for approximately two hours immediately before use.

Dead spaces were measured at 0°C using pure helium. It was assumed that helium obeys the ideal gas laws.

Nay (9), made corrections on all his measurements for the deviation of the gases used from ideality. He found such corrections could be neglected in this type of work.

All equilibrium pressure measurements were taken in the manner previously described. (Fig. 1)

No analysis of the gases was attemped. However, to ensure that impurities, such as air did not enter the system and to indicate the efficiency of the purification procedure, two quantities of each gas were separately purified and stored. Duplicate isotherms were then determined using each quantity of gas collected. Checks between the two isotherms were considered to indicate sufficient purity of gases.

Brunauer and Emmett (10), have proposed an empirical principle that true physical adsorption takes place near, or at the boiling point of the gas, since the Van der Waals' forces involved would be at a maximum. Accordingly, all isotherms were measured as near to the boiling point of the particular gas as possible without encountering capillary condensation. The temperatures at which the isotherms were measured are indicated below.

Adsorbate	B.P. (°C)	Isotherm at (°C)
Methane	-165	-145
Propane	- 42.2	- 39
Propylene	- 47.8	- 31
Butane	- 0.5	0
Isobutane	- 11.7	- 7
Butadiene-1,3	- 4.6	0
Cyclopropane	- 32.9	- 28
Neopentane	+ 9.4	+ 40
Acetylene	- 88.5	- 61
Nitrogen	-195.8	-190

RESULTS

Results

Langmuir type adsorption isotherms (equation (1)) of ten previously mentioned gases on nine charcoals were obtained in duplicate. Isotherms obtained for selected gases on certain charcoals are shown in Figs. 2 and 3. The significant data for all isotherms is included in Table I. Table I lists the volumes (V_m) of gases required to form monolayers on the adsorbents. Each value is an average of two measurements which were obtained from the slopes of the duplicate isotherms.

Table II shows the effective molecular adsorption areas of the adsorbates for each charcoal. They were calculated using equation (2). The effective adsorption area of the reference gas, nitrogen, was assumed to be 16.2 $\text{A}^{\circ 2}$.

Table III lists the surface areas of the charcoals available to each adsorbate. They were calculated using the relationship:

$$\text{Surface Area} = \frac{V_m N \sigma}{224} \times 10^{+2} \quad \frac{\text{meters}^2}{\text{gram}}$$

where: V_m = volume of gas in a monolayer. (in ml. (S.T.P.)

N = Avogadro's number.

σ = effective molecular adsorption area of the adsorbate in $\text{A}^{\circ 2}$

Trends in the "equilibrium" times indicated by point b in Fig. 1 are shown in Fig. 4. Table III (a) shows the times indicated by point p in Fig. 1 and the volumes of gases adsorbed, for each step in certain isotherms.

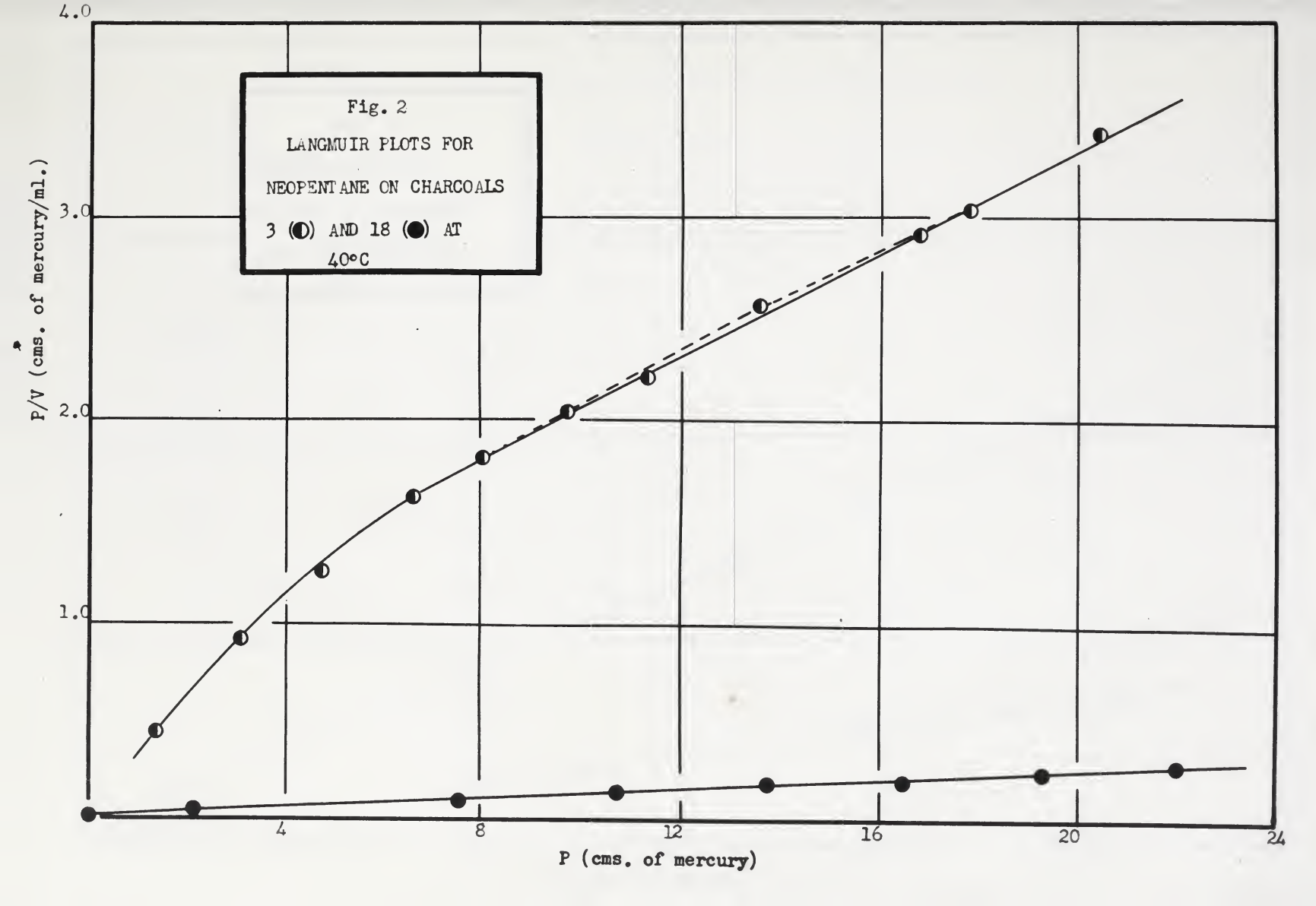


Fig. 2
LANGMUIR PLOTS FOR
NEOPENTANE ON CHARCOALS
3 (◐) AND 18 (●) AT
40°C
P/V (cms. of mercury/ml.)
4.0
3.0
2.0
1.0
4
8
12
16
20
24
P (cms. of mercury)

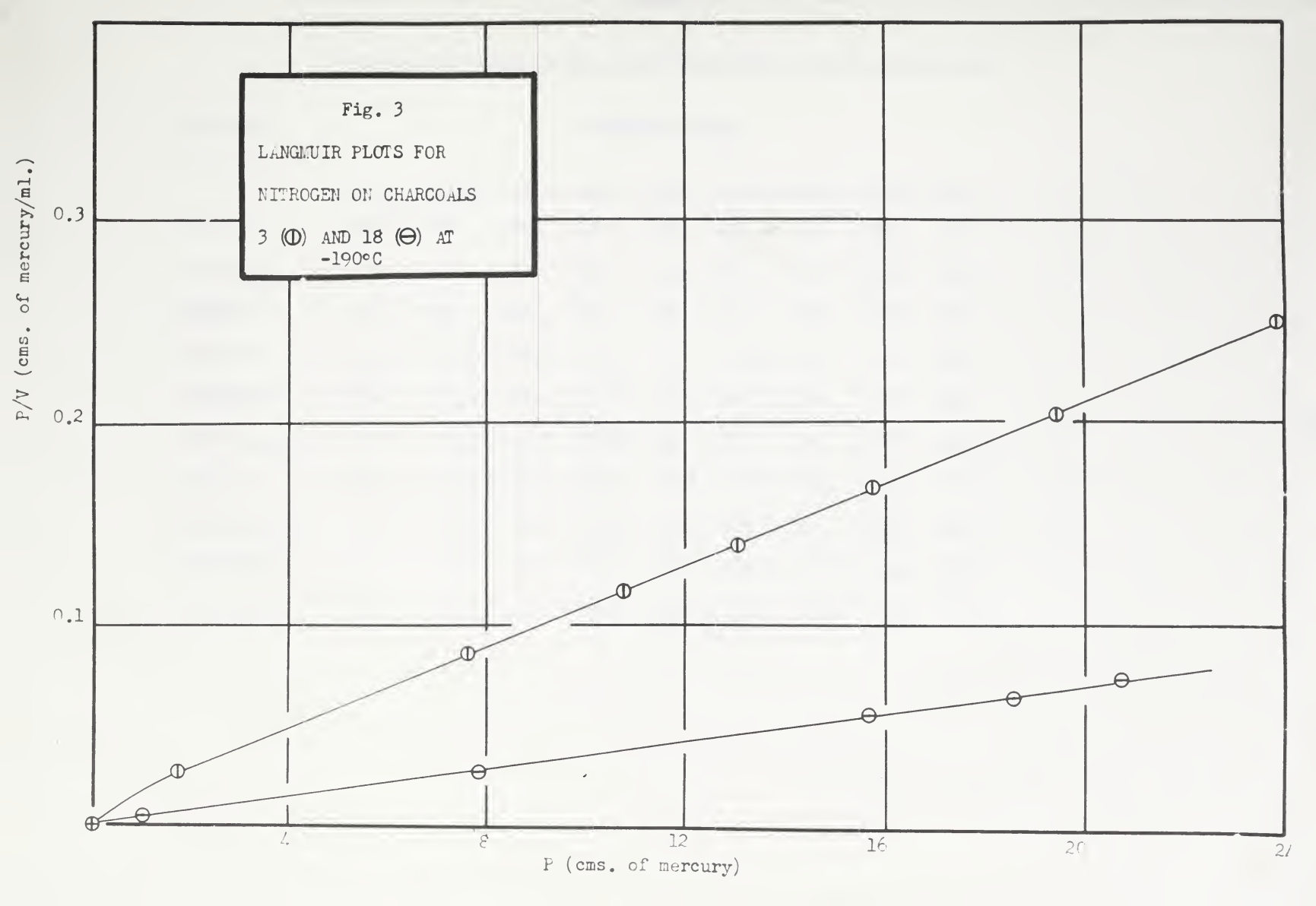


Fig. 3
LANGMUIR PLOTS FOR
NITROGEN ON CHARCOALS
3 (◑) AND 18 (⊖) AT
-190°C
P/V (cms. of mercury/ml.)
0.3
0.2
0.1
4
8
12
16
20
P (cms. of mercury)

Table I

Maximum Adsorption of Gases in Milliliters per Gram of Charcoal

Adsorbate	Charcoal Number								
	3	6	9	12	13	15	17	18	19
Nitrogen	98.5	150	182	187	198	253	283	283	277
Acetylene	87.5	116	131	138	154	186	210	203	196
Methane	88.2	129	146	153	178	209	231	236	237
Propane	31.6	61.0	79.4	84.2	91.4	98.5	113	121	112
Propylene	55.6	72.9	87.4	99.8	104	128	133	138	131
Cyclopropane	33.8	67.0	99.0	98.2	106	151	131	182	150
Butane	29.4	52.9	64.4	69.6	75.2	95.8	100	104	93.0
Butadiene-1,3	54.6	64.4	81.8	83.0	90.9	110	118	127	112
Isobutane	12.4	35.1	47.7	55.8	67.4	87.2	94.5	96.5	89.6
Neopentane	5.1	10.1	25.4	31.0	42.5	62.7	69.8	72.6	61.8

Table II

Effective Molecular Adsorption Areas in A^{o2}

Adsorbate	Charcoal Number									
	3	6	9	12	13	15	17	18	19	Average
Acetylene	18.2	20.9	22.5	21.9	20.8	22.0	21.8	22.6	22.9	22.3
Methane	18.1	18.8	20.2	19.8	18.0	19.6	19.8	19.4	18.9	19.7
Propane	50.5	39.8	37.2	36.0	35.1	41.6	40.6	37.9	40.1	40.5
Propylene	28.7	33.3	33.7	30.4	30.8	32.0	34.5	33.2	34.2	34.2
Cyclopropane	47.2	36.3	39.8	30.8	30.3	27.1	35.0	25.2	29.9	30.2
Butane	54.2	45.9	45.8	43.5	42.6	42.7	45.8	44.1	48.2	45.8
Butadiene-1,3	29.2	37.7	36.0	36.5	35.3	37.3	38.8	36.1	40.1	36.2
Isobutane	129	69.2	61.8	54.3	47.6	47.0	48.5	47.5	50.1	47.8
Neopentane	313	240	116	97.7	75.4	65.4	65.7	63.2	72.6	65.5

Table III

Surface Areas of Charcoals in $\frac{\text{meters}^2}{\text{gm.}}$

	Charcoal Number								
Adsorbate	3	6	9	12	13	15	17	18	19
Nitrogen	429	653	792	813	861	1101	1231	1231	1205
Acetylene	525	696	785	827	923	1115	1259	1217	1175
Methane	467	683	773	810	943	1107	1224	1250	1255
Propane	281	543	707	749	813	877	1006	1077	997
Propylene	511	670	804	918	956	1176	1222	1268	1204
Cyclopropane	274	544	804	797	861	1226	1064	1478	1218
Butane	362	652	793	857	926	1180	1232	1281	1146
Butadiene-1,3	531	627	796	808	885	1071	1149	1236	1090
Isobutane	159	451	613	717	866	1120	1214	1240	1151
Neopentane	90	178	447	546	748	1104	1229	1278	1088

Fig. 4.

EQUILIBRIUM TIME TRENDS

Time(minutes) vs.

Volume Adsorbed.

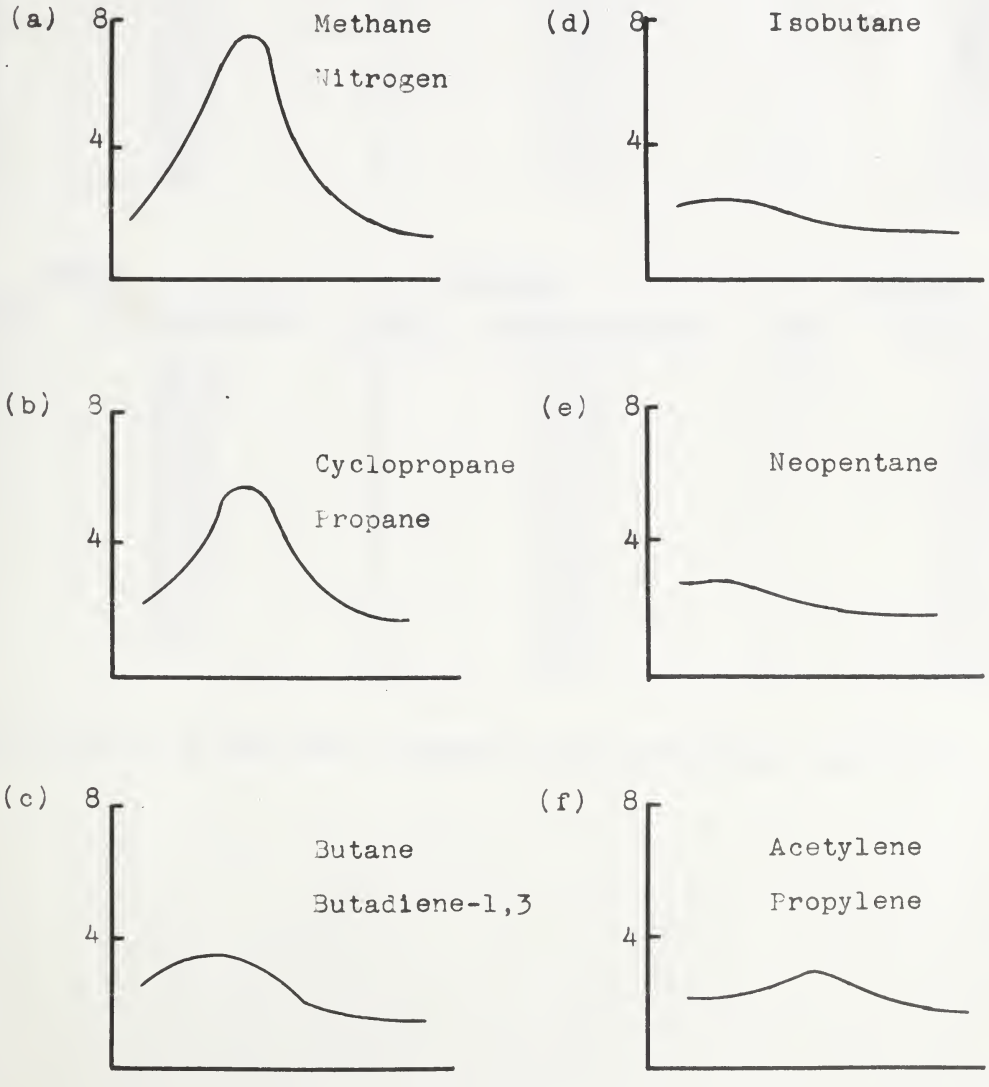


Table IIIa - Selected Equilibrium

Time Data

Time in minutes - Vol. adsorbed in $\frac{ml}{gm}$ (S.T.P.)

Methane		Propane		Propylene	
Time	Volume Adsorbed	Time	Volume Adsorbed	Time	Volume Adsorbed
3	16.6	2	17.2	2	29.06
4	46.26	3	37.3	2	49.66
6	94.70	5	49.01	3	61.95
8	119.7	2	51.66	2	67.50
3	122.1	2	53.33	2	71.53
3	125.3	2	54.66	2	74.09
3	125.5	2	55.54	2	76.59
2	127.1	2	56.16	2	78.37
2	129.4	2	57.13	2	79.15
2	130.2	2	57.70	2	79.89
2	130.2	2	57.88	2	81.67
2	130.2	2	58.63	2	81.91

Butane		Isobutane		Neopentane	
Time	Volume Adsorbed	Time	Volume Adsorbed	Time	Volume Adsorbed
2	30.43	2	23.20	2	7.33
3	53.59	3	38.59	2	8.52
3	57.32	2	42.58	2	8.96
2	58.41	2	43.56	2	9.53
2	59.39	2	44.74	1	10.02
2	61.16	2	45.13	1	10.55
2	61.60	2	46.21	1	11.12
2	62.68	2	46.56	1	11.61
2	63.13	2	46.76	1	12.09
2	64.45	2	47.59	1	12.72
2	65.24	2	48.28	1	12.94
2		2	49.16	1	13.02

The data given in this table is typical of the relationships shown in Fig. 4.

DISCUSSION OF RESULTS

Discussion of Results

Table I shows the volumes of the gases (S.T.P.) required to form a monolayer on the charcoals. The application of this data follows:

I Effective Molecular Adsorption Areas

The average effective molecular adsorption areas for each gas are based on the underlined values in Table II which appeared to be limiting values. The average of the selected values should be such that the surface area of the charcoal calculated from it is close to that computed from the molecular adsorption area assumed for nitrogen.

The use of 16.2 $\mathring{A}^2$ as the effective molecular adsorption area for nitrogen was based on measurements made at -196°C (5). All the nitrogen isotherms here were measured at -190°C. Livingston (6) indicates that 15.4 $\mathring{A}^2$ is a better value at -196°C. However, in view of the lower temperature used, 16.2 $\mathring{A}^2$ is probably the better value in this case.

Table IV shows data obtained by Nay and Morrison (3) for some of the gases used here on another series of charcoals.

Table IV

Effective Molecular Adsorption Areas in $\mathring{A}^2$

Adsorbate	Charcoal Number 1	2	3	4	5	6	7	8	Average
Acetylene	15.0	18.1	18.8	19.5	19.3	20.0	19.8	20.2	19.8
Methane	19.2	18.7	18.7	19.4	19.3	19.6	19.7	20.4	19.4
Propane	46.5	39.6	39.8	38.1	36.8	35.1	35.8	36.4	36.0
Butane	60.5	49.5	48.0	46.6	43.7	42.1	42.0	40.7	42.1
Isobutane	69.7	68.5	64.4	55.8	46.8	47.7	47.2	47.9	47.4

Nay and Morrison obtained this data on the basis of the effective molecular adsorption area of nitrogen being 16.2 $\mathring{A}^2$ at -190°C. With the exception of acetylene, their isotherms were measured at the same temperatures as those for the same gases used here. The author found evidence of capillary condensation at -75°C, the temperature at which Nay and Morrison measured the acetylene isotherm. Accordingly, -61°C was found to be the best temperature for the isotherm.

The data in Table IV shows certain trends. The effective molecular adsorption area of acetylene increases with increasing activation. For methane, it remains about the same, while for propane, butane, and isobutane, it decreases. Nay and Morrison have suggested that since acetylene is a thinner molecule than the reference gas, nitrogen, it can reach larger internal surfaces at lower activations, while at higher activations, both gases have access to the same surface. Accordingly, they presume that methane and nitrogen have access to the same surface throughout the series, and that propane, butane, and isobutane do not have access to the same surface as nitrogen until at higher activations.

The data in Table II show the same trends. The trends are less distinct than those in Table IV, especially for the thicker molecules. This indicates the presence of finer pores, capable of seiving the thicker molecules at higher activations. Morrison (11) has measured the adsorptions of several aliphatic acids on these charcoals and has noted similar erratic behaviour.*

This behaviour may affect the accuracy of the effective molecular adsorption areas, making it difficult to choose the best values for a good average.

* The behaviour of cyclopropane and propane suggests contamination of these gases.

Any comparisons of the values obtained here with existing data must be made between values measured at the same temperature and referred to the same molecular adsorption area of nitrogen. Also, it is preferable that the same type of adsorbent is involved.

Comparison of the values for methane, propane, butane, and isobutane, obtained by Nay and Morrison with those obtained here, shows excellent agreement in the cases of methane and isobutane. The molecular adsorption areas of propane and butane are slightly larger than those arrived at by Nay and Morrison.

Beebe, Polley, Smith, and Wendell (12) measured the molecular adsorption areas of butane on carbon blacks and obtained values ranging from 39.7 Å^2 to 45.1 Å^2. Emmett and Cines (13) found areas of 52 Å^2 and 41 Å^2 for butane on two zinc dusts. The same authors (14) assigned butane a value of 49 Å^2 on porous glass. For butane on various powders and metals, Davis, De Witt, and Emmett (15) assign butane a value of 46.9 Å^2. Butane on silica gel was found to have a molecular adsorption area of 46.5 Å^2 by Brunauer, Emmett, and Teller (16). Beebe, Kington, Polley and Smith (17) find the molecular adsorption area of butane on carbon black to be 45 Å^2.

For butadiene-1,3 on carbon black, Beebe and his co-workers (12) arrive at a molecular adsorption area of 32.9 Å^2.

Values of the molecular adsorption areas at different temperatures for some of the adsorbates used here are available and may be of interest.

Beebe, Kington, Polley, and Smith (17) have found the molecular adsorption area of neopentane on carbon black to be 57 Å^2 at 0°C. The value measured here was 65.5 Å^2 at 40°C. Emmett and Cines (14) found the value for acetylene on porous glass at -78°C to be 22.2 Å^2 as compared with the value found here at -61°C of 22.3 Å^2. Nay and Morrison (Table IV) assign acetylene a value of 19.8 Å^2 at -78°C.

The molecular adsorption area of propane on several aluminas at 0°C is 39 $\mathring{A}^2$ according to Russell and Cockran (18). The value measured here at -39°C is 40.5 $\mathring{A}^2$. Granquist (19) presents values of 25.6 $\mathring{A}^2$ and 27.8 $\mathring{A}^2$ for methane on Fuller's earth at -140°C as compared to 19.7 $\mathring{A}^2$ at -145°C, as measured here.

In general, the higher the temperature the larger the molecular adsorption area. Unsaturated molecules such as acetylene may behave strangely due to possible chemisorption. In view of this the above comparisons show that the values measured here vary in the right direction.

II Orientation of Adsorbate

Unsymetrical molecules usually have two possible orientations, vertical or horizontal. All of the gas molecules used in this work except nitrogen, methane, and neopentane are unsymetrical molecules. Of the three exceptions, methane and neopentane are perfectly symetrical. Nitrogen is usually considered to be a spherical molecule and therefore similar to methane. Unsymetrical molecules such as acetylene, butane, butadiene-1,3, propane, propylene, and isobutane may orient themselves on the adsorbent with their long axes parallel to the surface. This is horizontal orientation. If oriented vertically, the long axis is normal to the surface.

Cyclopropane also has two orientations, one with the plane of the ring parallel to the surface of the adsorbent, and the other with the ring normal to the surface.

Nay and Morrison (3) have suggested that the orientation of the adsorbate is an important factor in this work. They propose that if

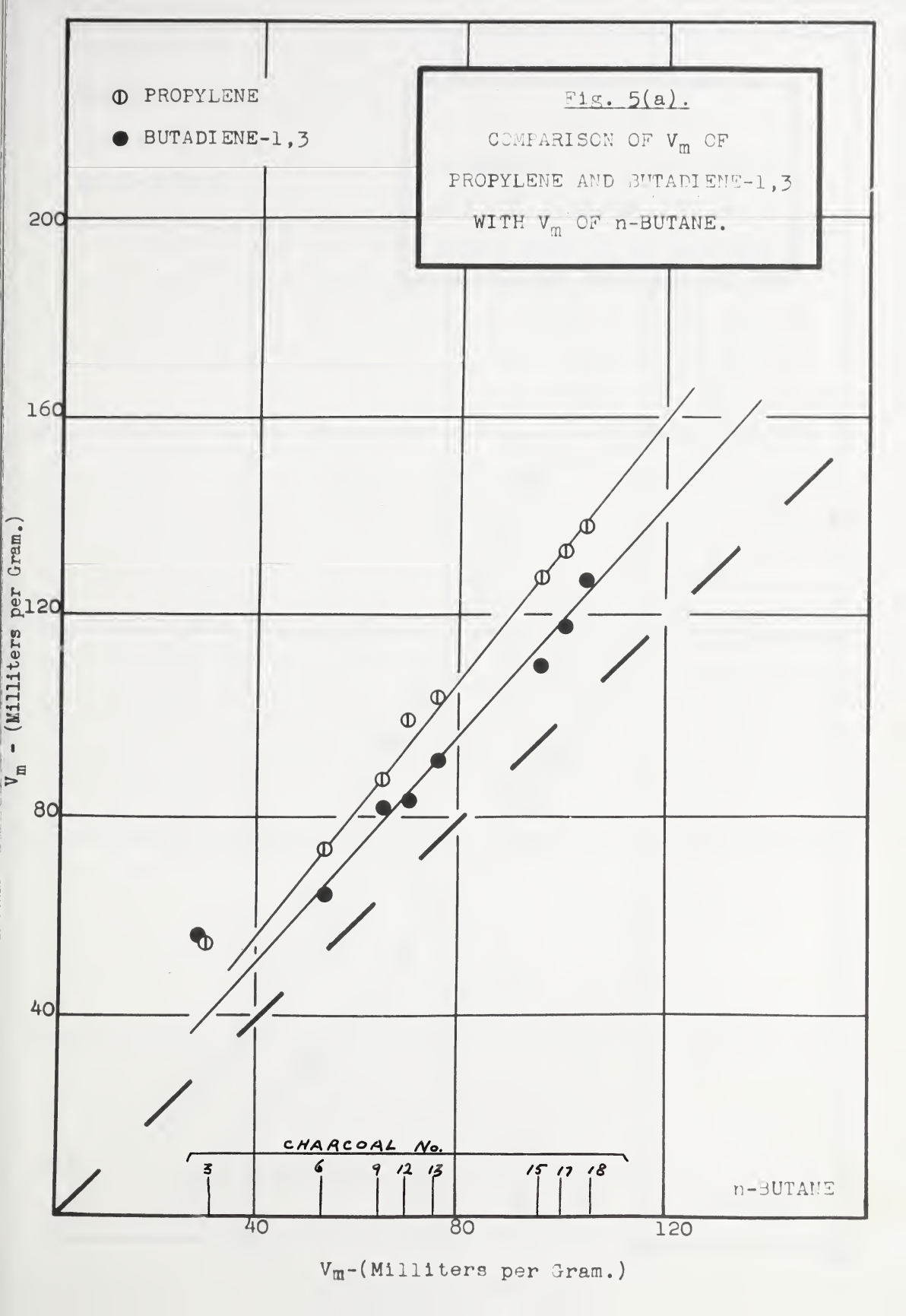
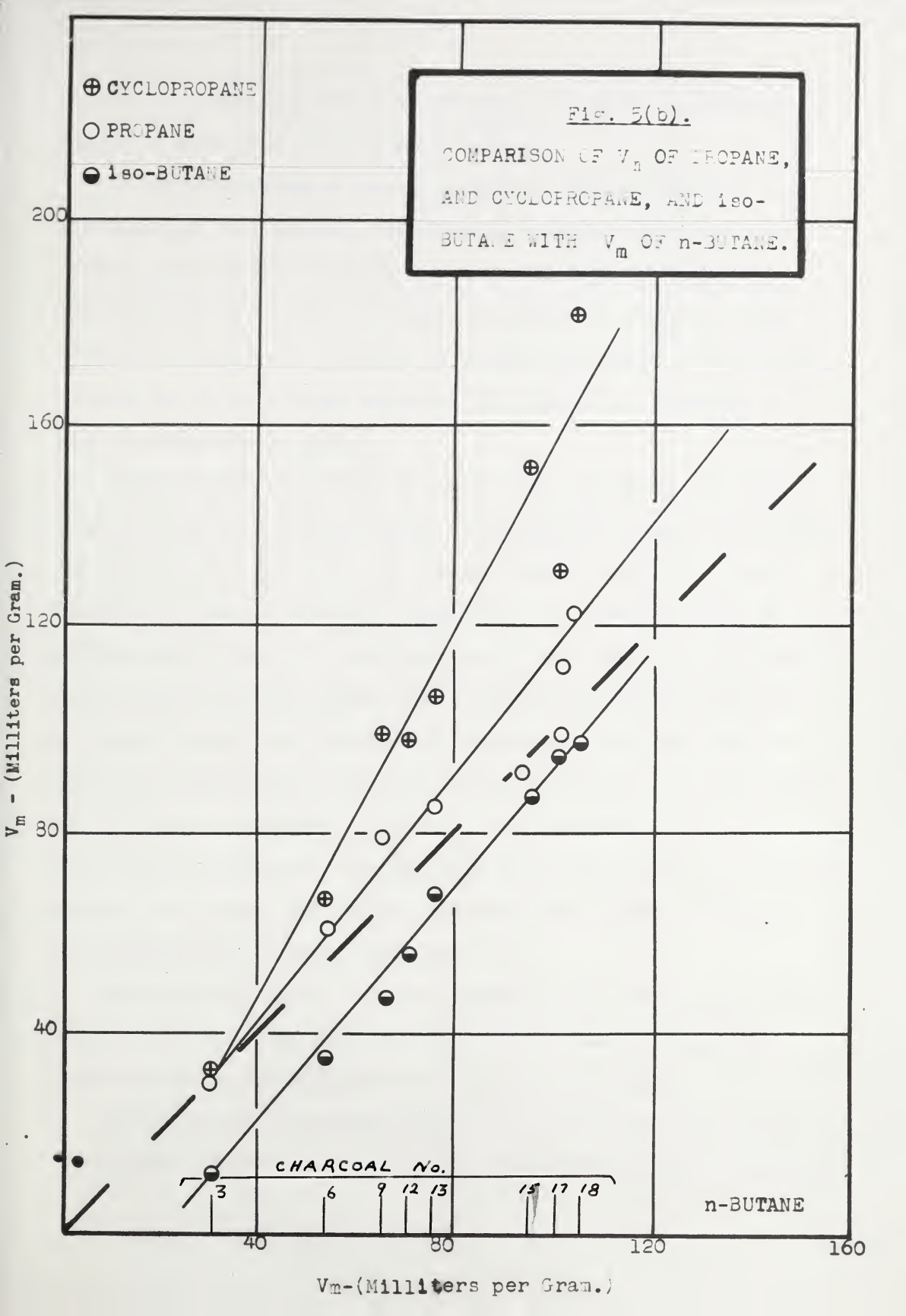


Fig. 5(a).
COMPARISON OF V_m OF PROPYLENE AND BUTADIENE-1,3 WITH V_m OF n-BUTANE.
PROPYLENE
BUTADIENE-1,3
200
160
120
80
40
V_m - (Milliters per Gram.)
CHARCOAL No.
3
6
9
12
13
15
17
18
n-BUTANE
40
80
120
V_m-(Milliters per Gram.)


⊕ CYCLOPROPANE
○ PROPANE
◒ iso-BUTANE
Fig. 5(b).
COMPARISON OF V_m OF PROPANE, AND CYCLOPROPANE, AND iso-BUTANE WITH V_m OF n-BUTANE.
200
160
120
80
40
V_m - (Milliters per Gram.)
CHARCOAL No.
3
6
9
12
13
15
17
18
n-BUTANE
40
80
120
160
Vm-(Milliters per Gram.)

orientation is vertical entry into the pores is governed by molecular length; if horizontal, by molecular thickness.

If the orientations of propane, propylene, butane, isobutane, and butadiene-1,3, were vertical, the effective molecular adsorption areas of these gases should be similar to that for methane. However, the molecular adsorption areas are larger the longer the molecule, hence horizontal orientation. Acetylene is a longer and thinner molecule than methane, yet it has a larger molecular adsorption area. Therefore it must be oriented horizontally.

Lemieux and Morrison (20) have compared the adsorptions of several aliphatic acids on a charcoal series. They proposed a method to elucidate the orientation of the acids. This method has been applied to gaseous adsorbates by Nay and Morrison. In it the V_m for a particular gas is plotted against the V_m of a reference gas for each charcoal. The linear plots obtained are then compared with a plot of the V_m for the reference gas against itself. Nay and Morrison indicate that the gases involved must be of similar cross section and suggest that lines of a slope greater than one indicate horizontal orientation, while parallel or coincident lines show vertical orientation. On this basis they presumed butane, propane, and ethane to be oriented horizontally, and infer that acetylene, ethylene, and isobutane have the same orientation.

The gases used in this work were compared in the same manner. It is indicated in Fig. 5 that cyclopropane, propane, butane, butadiene-1,3, isobutane, and possibly propylene are oriented horizontally.

The horizontal and vertical orientations of all these gases except cyclopropane are quite distinct. In the case of cyclopropane, a considera-

tion of its molecular model will show that it has two possible orientations. If it is oriented with the ring parallel to the surface of the adsorbent, the model will show that two thicknesses are involved. If the ring is normal to the surface, then the thickness involved is the same as one of the thicknesses associated with the other orientation. Both of the molecular adsorption areas and the three thickness/es are similar. The fact that a best fit straight line of slope greater than one was obtained for several of the points (Fig. 5) in the plot of V_m for cyclopropane versus V_m for butane indicates only that the molecular adsorption area of cyclopropane is smaller than that for butane. In view of the rotation of the methyl groups in a butane molecule, and the similarity of the cross-sections of cyclopropane, it would be difficult to establish the orientation of cyclopropane by the above method.

The behaviour of neopentane can be used to indicate the orientation of some of the other adsorbates. Consideration of the structures of neopentane and propane will reveal that propane is as long as the former is wide. If propane were oriented vertically, its length would determine its entry into the pores. It would therefore be excluded from the same internal surfaces as neopentane. The surface areas of each charcoal which are available to each gas are shown in Table III. They show that propane has access to much more surface than neopentane, except at higher activations. Therefore, propane and,propylene for the same reasons,are oriented horizontally. Molecules which are longer than neopentane is wide should have access to less surface than neopentane if oriented vertically. Such is not the case at lower activations. Hence, butane, butadiene-1,3, and isobutane are oriented horizontally.

Acetylene is a longer molecule than methane is thick. The former reaches larger internal surfaces than methane, as shown in Table III. Accordingly, acetylene must be oriented horizontally.

III Screening and Molecular Thickness

It has been indicated that acetylene, propane, propylene, butane, butadiene-1,3, and isobutane are oriented horizontally. Nay and Morrison (3) have suggested that in such a case the molecular thickness determines the accessibility of the absorbate to the internal surfaces of the charcoals.

The trends of the molecular adsorption areas shown in Table II support their suggestion. Molecules which are thicker than nitrogen, such as neopentane, isobutane, and cyclopropane show decreasing effective molecular adsorption areas as activation increases. This indicates that at lower activations, where the proportion of finer pores is greater, these molecules are being screened. The screening is very evident for neopentane. Accordingly, molecules which are longer than neopentane is thick, and molecules whose lengthsare similar to the thickness of neopentane, should show more pronounced or similar trends, respectively. For the former case, such molecules are isobutane, butadiene-1,3, and butane. The latter case involves propane and propylene. The trends for none of these adsorbates is similar in magnitude to that for neopentane. It is apparent then that molecular thickness governs the accessibility of these adsorbates to the internal surfaces of the pores.

Acetylene is a longer molecule than methane. Methane is approximately the same size as nitrogen, as evidenced by the fairly constant effective molecular adsorption areas of methane throughout the series. The molecular adsorption area of acetylene increases as activation increases. This indicates that it has greater access to internal surfaces than nitrogen. The suggestion is then, that its thickness determines its access to the pores.

The nature of the cyclopropane molecule does not permit evaluation of its effects in screening.

The trends in the surface areas of the charcoals, shown in Table III, illustrate the screening effect. They show that molecules which are thinner than nitrogen have access to greater internal surfaces at lower activations, while thicker molecules do not reach the same internal surfaces. As activation increases, the relative numbers of finer pores decreases. This is shown by the fact that all adsorbate molecules except propane and cyclopropane reach the same internal surfaces at higher activations. This was also indicated by Nay and Morrison (3) who made measurements with nitrogen, acetylene, methane, ethane, ethylene, propane, butane, and isobutane.

The areas of the various charcoals which are available to methane and nitrogen are similar throughout the series. This is due to their similar size.

Charcoal no. 19 shows certain peculiarities and will be discussed later.

IV Diffusion

Figs. 2 and 3 show the Langmuir isotherms obtained for neopentane and nitrogen respectively, on charcoals 3 and 18.

Nay and Morrison (3) have made measurements on another series of activated charcoals. Their measurements were made at higher pressures. The lowest pressure on any of their isotherms was in the neighborhood of 5 cms. of mercury. The author measured isotherms on a different series of charcoals at pressures as low as 1 cm. of mercury. Nay and Morrison extended their measurements to pressures in the vicinity of 50 to 60 cms. of mercury, and obtained about six points on the isotherms. The isotherms measured here extended to pressures of 30 to 40 cms. of mercury and were established by ten or twelve points.

Nay and Morrison noticed that for the larger adsorbate molecules, such as butane, on the lower activated charcoals, the isotherms obtained possessed a slight curvature, concave to the pressure axis. They suggested that the curvature was due to diffusion of the adsorbate into the finer pores of the adsorbent. The type of curvature described by Nay and Morrison is indicated by the dashed line in Fig. 2.

It was found that some of the isotherms obtained here showed a more pronounced curvature intially, as well as the slight curvature described by Nay and Morrison. The latter did not observe the pronounced initial curvature since their isotherms did not extend into the low pressure region where it occurs.

The initial curvature was more pronounced in the case of the larger adsorbate molecules and the lower activated charcoals. At higher activations it was not detectable in the case of the smaller adsorbates, such as nitrogen.

The slighter curvature described by Nay and Morrison behaved in a similar manner.

The portions of the isotherms obtained for neopentane and nitrogen on charcoals 3 and 18 are shown up to a pressure of 24 cms. of mercury in Figs. 2 and 3. Some of the initial points on the isotherms for nitrogen on charcoal 18 have been omitted since they were coincident (0 cms. of mercury). These isotherms show the two extremes in regard to the curvatures. The isotherms for other gases on intermediate charcoals showed curvatures between these extremes, dependent upon adsorbate size and charcoal activation.

The method proposed by Nay and Morrison for finding the equilibrium point (Fig. 1) is based on the assumption that the portion of the curve a b represents mainly adsorption. The pronounced initial curvature noticed here for some of the gases on certain charcoals suggests that a b represents mainly diffusion. The extent to which this diffusion will affect the isotherms has not been measured. Due to the higher initial pressures in the isotherms measured by Nay and Morrison, it is probable that there was more diffusion throughout their isotherms than contemplated. Here it appears that most of the diffusion occurred initially. Accordingly, the almost linear portions of the isotherms obtained here should be more representative of adsorption than those obtained by Nay and Morrison. This is indicated by a comparison of some of the values for the molecular adsorption areas obtained here with those measured by Nay and Morrison (Table IV). Indications are that there is more diffusion in the case of larger adsorbate molecules. This should result in lower values of the molecular adsorption areas. The values

measured by Nay and Morrison for propane and butane are lower than those obtained here. Accordingly, one would expect good agreement with the values obtained for smaller adsorbate molecules. Such is the case. (cf. methane).

V Equilibrium Times

Fig. 4 shows trends in the equilibrium times for the adsorbates used here. The equilibrium time referred to is that time which is indicated by point b in Fig. I. The curves shown in Fig. 4 were sketched according to the general trend of the times indicated by b for each point on the isotherm.

These trends were not observed by Nay and Morrison (3), probably because they measured their isotherms at higher pressures.

A distinctive feature shown in Figs. 4 (a,b,c,d, and e) is that the maxima in the curves decreases as the thickness of the adsorbate molecule increases. Indications are (Table III) that acetylene and propylene are thinner than nitrogen. Fig. 4 (f) shows a slight peak for these gases. It was noticed, that in general, the distinctive features (maxima, inflection points, etc.) of the curves for all adsorbates excepting neopentane became less pronounced and tended to shift to the right as activation increased.

These observations suggest that the shape of the curves is due to the pore structure of the charcoal and the ease with which an adsorbate may enter the various sized pores.

The diffusion effects previously discussed make further speculation on the nature of these curves difficult.

VI Charcoal 19 and Overactivation

Overactivation is a process in which the surface area of the charcoal decreases, probably due to the breaking down of pore walls. Charcoal 19 appears to be overactivated. Table III shows that it presents less surface to the larger adsorbate molecules, than charcoal 18, In the case of the smaller adsorbate molecules, there is no noticeable effect. This suggests that the larger pores are affected to a greater extent than the smaller ones.

Because of overactivation, charcoal 19 is unique in this series of charcoals. For this reason it has been omitted in Fig. 5. (V_m Plots)

SUMMARY

Nay and Morrison (3) have studied the adsorption of nitrogen, methane, ethane, propane, butane, isobutane, ethylene, and acetylene on a series of activated charcoals. Their work has been extended, using a different series of charcoals. In addition to nitrogen, methane, propane, butane, isobutane, and acetylene, the adsorption of butadiene-1,3, neopentane, cyclopropane, and propylene were investigated.

The molecular adsorption areas of these gases were measured and are presented in Table III.

All of the gases used here except methane, nitrogen, and cyclopropane appear to be oriented horizontally on the charcoal surface. The orientation of cyclopropane could not be determined due to structural factors. It has been shown that symetrical molecules of various sizes(neopentane and methane) are a great aid in indicating the orientation of unsymetrical molecules.

The suggestion of Nay and Morrison that screening is governed by molecular thickness in the case of horizontal orientation has been strenghtened by a

comparison of the behaviour of neopentane and methane with that of the other gases.

The diffusion process is suggested to be a more important factor than indicated by Nay and Morrison (3). On this basis, the method used here (low initial pressures) is suggested to give isotherms which are more representative of adsorption than the isotherms measured by Nay and Morrison.

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